

Abstract

Sugars and related polyols are critical components of all organisms and may have been necessary for the origin of life. To date, this class of organic compounds had not been definitively identified in meteorites. This study was undertaken to determine if polyols were present in the early Solar System as constituents of carbonaceous meteorites. Results of analyses of the Murchison and Murray meteorites indicate that formaldehyde and sugar chemistry may be responsible for the presence of a variety of polyols. We conclude that polyols were present on the early Earth through delivery by asteroids and possibly comets.

Sugar-Related Organic Compounds in Carbonaceous Meteorites

George Cooper*, Novelle Kimmich, Warren Belisle, Josh Sarinana, Katrina Brabham, Laurence Garrel,

G. Cooper, N. Kimmich, J. Sarinana, K. Brabham, W. Belisle,
NASA Ames Research Center, Moffett Field, CA 94035 USA

L. Garrel, current address, International Research School of Planetary Sciences (IRSPS), Università d'Annunzio Viale Pindaro, 42
65127 Pescara, Italy

Carbonaceous meteorites contain a diverse suite of soluble organic compounds. To date, these compounds provide the only record available for the laboratory study of organic chemical processes in the early Solar System. The Murchison meteorite is the best-characterized carbonaceous meteorite with respect to organic chemistry. The study of its organic compounds has been important in understanding aqueous processes on carbonaceous meteorite parent bodies chemistry as well as the formation of compounds of potential importance for the origin of life. Among the classes of organic compounds found in Murchison are amino acids, amides, carboxylic acids, hydroxy acids, sulfonic acids, phosphonic acids, purines and pyrimidines (1). These compounds such were quite likely delivered to the early Earth in asteroids and comets (2,3).

Notably absent among the classes of biologically important compounds accepted to be indigenous to carbonaceous meteorites are polyhydroxylated compounds (polyols) including sugars (polyhydroxy aldehydes or ketones), sugar alcohols and sugar acids. These compounds are essential in contemporary biochemistry: ribose and deoxyribose, five-carbon (5-C) sugars, are structural components of nucleic acids, RNA and DNA, and

glycerol, a three-carbon (3-C) sugar alcohol, is a constituent of all known biological membranes. Due to the reactivity of sugars, some researchers have questioned the life times of sugars under the presumed conditions on the early Earth and postulated other (more stable) compounds as constituents of the first replicating compounds or their precursors (4,5). The identification of potential sources and/or formation mechanisms of pre-biotic polyols would add to our understanding of what organic compounds were available, and for what length of time, on the ancient Earth. In this regard, meteorites serve as a model of what organic compounds were available abiotically in the early Solar System.

Earlier studies on the possible presence of sugars in (pre-Murchison) meteorites (6,7) reported glucose and/or mannose (6-C) in eight meteorites (predominately carbonaceous meteorites), much smaller amounts of arabinose (5-C) in three carbonaceous meteorites, and xylose (5-C) in an enstatite meteorite. These studies used thin-layer chromatography or UV-VIS detection. The authors also reported several amino acids in the same samples. However, with the exception of the Murray meteorite, all of the examined meteorites had fallen at least fifty years before the experiments thus increasing the chance of microbial contamination. The authors and a later reviewer (8) concluded that at least a portion of the identified compounds could have been contaminants.

The present study was intended to determine if soluble sugars, and polyols in general, are present in carbonaceous meteorites by using gas chromatography-mass spectrometry (GC-MS) as the means of identification. Results are reported from analysis of water extracts of the Murchison and Murray carbonaceous meteorites. Murchison, which fell in 1969, is generally regarded as the least contaminated carbonaceous meteorite. Murray, also a carbonaceous meteorite, has an organic compound content that is qualitatively similar to Murchison. Sample preparation and

purifications were, in some cases, similar to previous techniques and identification of compounds were done by derivatization to their trimethylsilyl (TMS) and/or tertiary butyl-dimethylsilyl (t-BDMS) forms (9).

Our analyses of Murchison and Murray extracts show that a variety of polyols are present in carbonaceous meteorites (Fig. 1). The identified compounds include a sugar, dihydroxyacetone; sugar-alcohols; sugar mono-acids; sugar di-acids; and “deoxy” sugar acids (or “saccharinic” acids). In general, the compounds follow the abiotic synthesis pattern of other meteorite classes of organic compounds (1): decreasing abundance with increasing carbon number within a class of compounds and many, if not all, possible isomers present at a given carbon number. Many of the compounds shown were positively identified by comparison of their mass spectra to commercially available standards (Fig. 2). Deoxy sugar acids were synthesized (below). Murchison and Murray are similar with respect to the presence of individual polyols.

Dihydroxyacetone, the only monomeric sugar identified in water extracts, was seen in all Murchison extracts and the Murray extract. It was relatively abundant in one Murchison sample (Fig. 3). In two of the Murchison extracts and the Murray extract the mass spectrum was weak (due to lower abundance) although it could be identified by ion searches for characteristic mass fragments (Fig. 2). In addition, analytical procedures using standards of dihydroxyacetone resulted in less than quantitative recoveries (in contrast to ribose) (9). If dihydroxyacetone was present due to contamination, e.g., microbial or soil, a wider array of sugars should also have been seen (10,11).

Results of analysis for the 2-C analog of dihydroxyacetone, glycolaldehyde, were inconclusive and further analyses are in progress. 6-carbon monomeric sugars were not seen in water extracts, however, we cannot rule out the presence of compounds

containing them as there was suggestive evidence (mass spectra) of their presence in di-compounds in the largest Murchison sample. These analyses are also in progress.

The so-called sugar alcohols begin with glycerol; however, the 2-C homologue, ethylene glycol, is also present and seen in both meteorites. The series begins with ethylene glycol and extends to at least C-6 members. These compounds were initially identified as their tBDMS derivatives based on comparison of their mass spectra and retention times to standards. Ethylene glycol and glycerol are the most abundant of all identified polyols. Glycerol is often, but not always, the most abundant member of the series. Concentrations of indicated polyols were determined by GC-MS and should be considered approximate as there is significant variation with sample. Glycerol is present in Murchison at approximately 160 nmole/gram, i.e., roughly double the highest concentration found for an individual meteorite amino acid (1). There is a significant drop in abundance from glycerol to higher C alcohols – the detector responses of threitol and erythreitol were approximately 100 times less than that of glycerol. 4-C and higher sugar alcohols are lower in abundance than all of the other (definitively) identified polyols.

Glycerol, as well as some of the other sugar alcohols, is widespread in nature and therefore a portion of the compound could be a contaminant either from analytical procedures (although none was seen in blanks) or from microbial action within the meteorite sample. However, given the relatively large amounts seen in all samples and the fact that the sugar alcohols are present in an abiotic distribution pattern makes it likely that a significant amount of the identified glycerol is indigenous to the meteorites. In this regard, the 4-C alcohol, erythritol, which is found in nature, and its rare isomer (12), threitol, are nearly equal in abundance in both Murchison and Murray. The 3-C “deoxy” sugar alcohols, 2, 3-propanediol and 1, 3-propanediol, were not seen in any sample.

This may be important from a synthetic point of view (below). Also identified in Murchison (as their TMS derivatives) were inositols, 6-C cyclic alcohols. However, they must be fully characterized as some of the nine possible stereoisomers are widely distributed in nature (13).

To determine the bulk isotopic content of neutral compounds, the neutral fraction of compounds from a Murchison extract, obtained by ion exchange chromatography, was acid hydrolyzed and re-fractionated (9). This resulted in the isolation of (predominately) sugar alcohols, i.e., ethylene glycol, glycerol, etc. The isotope values obtained were $\delta^{13}\text{C} = -5.89 (\text{‰})$ and $\delta\text{D} = +119 (\text{‰})$. These values are uncorrected for terrestrial carbon and hydrogen contributed during analytical procedures and thus should be considered lower limits. Even so, they lie outside the range of typical terrestrial organic compounds (14) and are consistent with values obtained for other classes of meteoritic organic compounds (1). This suggests that the majority of these compounds are indigenous to the meteorite. Isotopic analysis of individual polyols (in progress) may shed light on synthetic relationships among the various classes.

The sugar mono-acids (aldonic acids), begin with the 3-C member, glyceric acid and extend to at least the C-6 isomers (Fig. 1). The 2-C analog of glyceric acid, glycolic acid, as well as other mono-hydroxy acids, are well known constituents of carbonaceous meteorites (1). The abundance of glyceric acid, ~80 nmole/gram, is similar to that of the more abundant amino acids. The pattern of sugar acids is also abiotic, for example, 2-methyl glyceric acid (2-MGA), a relatively uncommon compound in nature, is also abundant. Its detector response (TMS derivative) was approximately one-sixth that of glyceric acid. Erythronic and threonic acids (~ 4 nmole/gram) were nearly equal in abundance in one Murchison extract (Fig. 3B), however, the ratio of

erythronic to threonic varied from approximately two to three in other samples and a glucose degradation experiment (below). The detector response of ribonic acid (TMS derivative) was roughly one-third that of threonic acid. Tartaric acid is the first member of the sugar dicarboxylic acid series. As with erythritol/threitol, tartaric acid (racemic) and its rare terrestrial isomer, meso tartaric acid, are nearly equal in abundance.

Deoxy sugar acids (Fig. 1B), or “saccharinic” acids in the context of sugar chemistry, usually refer to polyhydroxylated organic acids in which one or more hydroxyl groups (bonded to C) is replaced by hydrogen. The deoxy acids in Fig. 1B are less common in nature than sugars and laboratory standards are not available commercially; however, they are well known products of alkaline reactions of sugars (13,15,16). In this study, they were synthesized by known methods of alkaline degradation of 6-C sugars; 2-deoxy 5-C and 6-C acids (Fig. 1B) were also synthesized by acid oxidation of the corresponding 2-deoxy sugars (9). Their TMS and tBDMS mass spectra were then compared to compounds in both meteorites and (TMS derivatives) to literature spectra (17). In the largest Murchison sample the detector responses of the 4-C members were roughly 4-5 times higher than those of the 4-C mono-acids (erythronic and threonic).

There are two possible (excluding enantiomers) straight chained 5-C 2-deoxy mono acids (2-deoxypentonic acids) and both are apparently present in Murchison. Due to low abundances quantitation was not possible, however, their detector responses were roughly twenty times less than that of ribonic acid. 2-deoxyhexonic acids as well as 5-C and 6-C deoxy dicarboxylic acids may also be present, however, due to their low abundances and resulting lower quality mass spectra, their presence cannot yet be confirmed. Compounds of matching GC retention times and apparently of the same molecular weights (tBDMS derivatives) are seen. In any case their abundances would be well below those of the 5-C and 6-C mono-acids (ribonic, gluconic, etc.). In

Murchison, a 3-deoxyhexonic acid (a "metasaccharinic" acid) was identified (Fig. 1); its detector response was approximately equal to that of the 2-deoxypentonic acids. At least one 3-deoxypentonic acid is tentatively identified, the detector response(s) is clearly less than that of the 3-deoxyhexonic acid. Other, unidentified, compounds with TMS mass spectra similar to those of deoxy sugar acids (17) are also present. These could include branched deoxy acids.

A plausible synthetic origin for at least of some of the polyols in Murchison and Murray involves the photolysis of interstellar gases on interstellar grains. Laboratory experiments intended to simulate interstellar/solar system processes (18,19) have shown that a variety of relatively low molecular weight compounds are formed from the low temperature (<100K) UV photolysis of frozen gases (CO, NH₃, H₂O, etc.) known to be interstellar medium (ISM) constituents. When such photolyzed ices are allowed to warm some of the identified compounds (also observed in this work) are glycerol, glyceric acid, and ethylene glycol. In addition, there is evidence that photolysis may have played a role in the synthesis of other meteoritic compounds (20). Some compounds produced in the photolysis experiments have not been found in carbonaceous meteorites. However, in general, compounds in the higher molecular weight range of the present compounds have not reported from such experiments.

Another possible mode of synthesis of the meteoritic polyols involves the aqueous chemistry of formaldehyde. The most generally agreed upon mechanism for natural abiotic synthesis of sugars is the "formose" reaction (21). In laboratory formose reactions, formaldehyde (CH₂O), in aqueous solution at neutral to basic pH, reacts to produce a variety of hydroxylated compounds, predominately sugars, of carbon number up to at least seven. Several lines of evidence suggests that the formose reaction would have been possible on the parent bodies of carbonaceous meteorites: aqueous alteration occurred on the parent bodies

and/or precursor interstellar ices (22,23); water extracts of carbonaceous meteorites are commonly slightly basic (pH ~ 7-9); formaldehyde is a relatively abundant and ubiquitous molecule in interstellar space and comets (24); several small volatile carbonyl compounds are constituents of Murchison (25); and glycolaldehyde, necessary to form higher sugars in the formose reaction, has recently been identified in interstellar space (26). In addition, the condensation product (cyanuric acid) of another interstellar molecule, isocyanate (OCN), has been identified in Murchison (27,28) as well as possible isocyanate reaction products (28).

As mentioned above, alkaline conditions also alter and decompose sugars. If, in addition to dihydroxy acetone, other sugars were also initially present on the meteorite parent body, their current absence (or low relative abundance) may be a consequence of the limited lifetime of sugars under basic conditions (29,15). The sugars may have undergone various reactions including oxidation to acids of the corresponding carbon number, e.g., ribose to ribonic acid (Fig.1). Fragmentation of sugars to mono-hydroxy acids of lower carbon number (formic, glycolic, lactic, etc.) is an important process in alkaline solution (16). Such acids are relatively abundant in carbonaceous meteorites (1) however we cannot state what percentage, if any, of these (or mono-hydroxy di-acids) were contributed by such decomposition processes. Alpha-hydroxy as well as non-alpha hydroxy acids are produced in such reactions. The sugar-acids may have also been synthesized by the mechanism(s) that synthesized the mono-hydroxy acids of carbonaceous meteorites.

Meteoritic deoxy sugar acids (Fig.1B) are consistent with the presence of sugars in alkaline aqueous solution. These compounds are well known products of the alkaline alterations of sugars. They have been reported to constitute as much as 10-30% of the alkaline degradation products of sugars (16). Unlike the other 4-C deoxy acids (Fig. 1B), 2,3-dihydroxybutyric acid is rarely

mentioned as a sugar reaction product. It has been identified in the alkaline degradation of polysaccharides from wood pulp (30) where its concentration was approximately equal to that of 3, 4-dihydroxybutyric. In our degradations of glucose there is only a trace of one of the two isomers (at 21.24 min. in Fig 3C) - found only after searches for characteristic mass spectral ions 203, 220, and 292 (TMS derivatives). Consistent with previous studies, we found that 2, 4-dihydroxybutyric acid was a major product of alkaline degradation of glucose (Fig 3C). The conditions typically used in lab experiments are of course not likely to match those in place during formation of meteorite organic compounds. For example, the majority of the above-mentioned alkaline sugar experiments were conducted using alkaline earth hydroxides which resulted in pH values above those likely for the meteorite parent body. However, qualitatively, reactions of organic compounds in basic pH and low temperature are plausible meteoritic conditions (22). The extent of parent body reactions under these conditions may account for the differences in the ratios of compounds between experiments and those observed in the meteorites, e.g., 3-deoxyhexonic acids are relatively abundant in the glucose experiments (Fig 3C) but relatively minor products in Murchison. It should be noted that if alkaline alteration of sugars was actually the principal mode of formation of the meteoritic deoxy acids there was not necessarily a need for the initial presence of deoxy sugars, e.g., 5-C deoxy sugars would not have been required to give 5-C deoxy acids (Fig. 1). Deoxy-sugars have not been reported in formose reactions and, as mentioned above, deoxy sugar alcohols (3-C) were not seen in the present study.

The above scenarios are two of what may be multiple mechanisms capable of producing meteoritic polyols. Whatever the mode of synthesis, polyols or similar material are a significant fraction of meteoritic organic carbon. The majority of organic carbon in carbonaceous meteorites is bound in an insoluble

“macromolecular” or “polymeric” carbon phase (1). Recent research employing ^{13}C NMR to study the macromolecular carbon of Murchison has demonstrated that as much as 5% of this carbon has hydroxy and/or ether (C-O-C) bonds (31). Carbonyl bonds (other than those in carboxylic acid groups) are also significant. If formaldehyde condensation was a source of meteoritic polyol monomers then it may have also contributed to the solid phase.

The fact that a large suite of related sugar derivatives, sugar decomposition products, and the smallest sugar, are present in the Murchison and Murray carbonaceous meteorites makes it likely that more sugars, at one time, were also present. Other bodies (comets or asteroids), perhaps in less advanced stages of aqueous alteration or oxidation, may have delivered intact sugars or formaldehyde to planets in the early solar System. However dihydroxyacetone in the presence of minerals is capable of producing higher sugars in aqueous solution (32). As a model of prebiotic chemistry, the finding of these compounds in some of the oldest objects in the Solar System suggests that polyhydroxylated compounds were, at the very least, available for incorporation into the first living organisms.

Figure captions:

Figure 1A. Polyols identified in the Murchison and Murray carbonaceous meteorites. Compounds were identified by gas chromatography-mass spectrometry (GC-MS) as their trimethylsilyl (TMS) and/or tertiary butyl-dimethylsilyl (t-BDMS) derivatives (9) (Fig. 2). Some of the acids were also identified in their cyclic (lactone) form. When commercial standards were not available for mass spectral comparison, some of the compounds under a category of “isomers” were identified by comparison of their mass spectrum and GC retention time to that of the listed member of the group. *6-C Sugars monomers were not seen but may be present in bound forms.

Figure 1B. Deoxy sugar acids in Murchison and Murray.

†Identifications of 2-deoxyhexonic acids and deoxydicarboxylic acids are tentative (see text). The analyses were stopped at 6-C compounds although there is suggestive evidence of compounds of higher carbon number.

Figure 2. Selected mass spectra of *t*BDMS and TMS derivatives of standards and corresponding compounds (of the same GC retention times) from the Murchison and Murray meteorites.

Dihydroxyacetone is derivatized as di-*t*BDMS; 2-methyl glyceric acid as tri-TMS; threonic acid as tri-*t*BDMS; and ribonic acid as tri-*t*BDMS. Ribonic acid was also identified as the lactone.

*t*BDMS derivatives give a characteristic molecular ion minus 57 amu peak ($M^+ - 57$), e.g., dihydroxyacetone(*t*BDMS)₂ = 318 amu therefore, $M^+ - 57 = 261$ (a further loss, probably H₂CO, yields a fragment of 231 amu). *t*BDMS derivatives have been used previously in other applications (33) including analysis of organic compounds in Murchison (28). TMS derivatives give a characteristic $M^+ - 15$ peak among others. Mass spectra of sugar derivatives have been described in detail (17).

Figure 3A. Dihydroxyacetone and glycerol from segment of a GC-MS total ion chromatogram (TIC) of neutral (water soluble) compounds from the Murchison meteorite.

Figure 3B. A portion of the TIC of acidic compounds (tBDMS derivatives) from Murchison. Malic acid and other hydroxy acids and pyroglutamic acid are known constituents of Murchison (1).

Figure 3C. Reaction products (TMS derivatives) from alkaline reactions of glucose (9) : (1) glycerol; (2) ethylene glycol; (3) 2-methyl glyceric acid; (4) glyceric acid; (5) succinic acid; (6) 2,4-dihydroxybutyric acid; (7) threonic acid; (8) erythronic acid; (9, 10) 3-deoxyhexonic acids (6C); (11, 12) lactones of 3-deoxyhexonic acids.

References

1. J. R. Cronin and S. Chang, in *Chemistry of Life's Origins*, J. M. Greenberg, V. Pirronello, and C. Mendoza-Gomez, Eds. (Kluwer, Netherlands, 1993), pp. 209-258.
2. E. Anders, *Nature* **342**, 255 (1989).
3. C.F. Chyba and C. Sagan, *Nature* **355**, 125 (1992).
4. K. E. Nelson, M. Levy, S. L. Miller PNAS **97**, 3868 (1997).
5. A. W. Schwartz and R. M. de Graaf, *J. Mol. Evol.* 36???, 101 (1993).
6. E. T. Degens and M. Bajor, *Naturwissenschaften* **49**, 605 (1962).
7. I. R. Kaplan, E. T. Degens, J. H. Reuter, *Geochimica et Cosmochimica Acta* **27**, 805 (1963).
8. J. M. Hayes, *Geochimica et Cosmochimica Acta* **31**, 1395 (1967).
9. Identification of compounds are from multiple extracts of Murchison. One sample of the Murray meteorite (4 grams) was used. In some cases, sample extraction and preparation procedures, included separating compounds by acidity, are similar to those used previously (28,20). In the most recent Murchison samples, extractions were done under helium (99.999%). Cation exchange procedures were as previously described. Anion exchange resins were either Biorad AG4-X4 (OH⁻ form) or Biorad AG1-X8 (acetate form). All samples were dried by rotary evaporation with further drying by the addition and evaporation of

dichloromethane. Preparation procedures gave quantitative yields of ribose and ribonic acid standards but dihydroxyacetone yields could be as low as 50 %.

All compounds were identified as their *tert*-butyl dimethylsilyl (tBDMS) and/or trimethylsilyl (TMS) derivatives by gas chromatography-mass spectrometry (GC-MS). Derivatization reagents were N-Methyl-N-(*tert*-butyldimethylsilyl)trifluoroacetamide with 1% *tert*-butyldimethylsilyl chloride, Regis Chemical Co., (to obtain tBDMS derivatives) and Bis(trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane, Alltech Assoc., for TMS derivatives. tBDMS derivative preparation of the dried samples was similar to previous techniques (28) except that in the majority of the present preparations (tBDMS and TMS) pyridine was used as the solvent in a ratio of 4/1 (pyridine/reagent). BSTFA/pyridine solutions were sonicated from ~ 5-30 min and were stored up to 1 hour in a desiccator at room temperature before the first analysis. Some TMS solution were also heated (~ 15 minutes at 60°C) after sonication. Each sample was analyzed multiple times – each with increasing concentration (by evaporation). TMS derivatization generally results in fewer peaks on a chromatogram due to quantitative derivatization of active sites. In some cases, even when the degree of derivatization was the same, it was found that TMS derivatization resulted in higher sensitivity for individual standards. tBDMS derivatives generally give more reliable molecular weight information, i.e., the ($M^+ - 57$) ion (Fig. 2) and were much more stable when samples were concentrated for GC injection.

In alkaline degradation of sugars individual sugars were heated in 1-8M NaOH for between 5 minutes and 2 hours. The glucose sample in Fig. 3C was heated for 5 min. at 80 °C. After heating the samples were passed through a column of AG50 X-4 cation exchange resin, eluted with water, dried, and derivatized. 2-

Deoxyribonic acid and 2-deoxygluconic acid standards were obtained by HNO_3 oxidation of 2-deoxyribose and 2-deoxyglucose, respectively. Deoxy 5-C and 6-C meteoritic acids were analyzed in their straight-chain form by bringing the sample containing them to slightly basic pH with sodium hydroxide or ammonium hydroxide.

In the majority of GC-MS analyses a Finnigan ion trap GCQ GC-MS (70 eV) was used. A DB-17 (30 m x 0.25 mm) or DB-17ms 60 m x 0.25 mm fused silica capillary column (J & W Scientific, DB-17) was used for separations. Commonly used operating conditions were: initial temperature, 70°C; ramp rate, 3°C/minute to 240°C, hold 1 hour; interface temp., 260°C; detector temp., 200°C. For quantitation (approximate) of compounds, single ion monitoring (SIM) as well as full scan mode was used for representative mass fragments.

Isotope measurements of neutral compounds. Neutral compounds, including amides, were obtained by ion exchange chromatography of a Murchison extract as described previously (28). Polyols were isolated by acid hydrolysis (HCl) and re-subjecting the fraction to cation and anion exchange chromatography to remove resulting acids (and possible basic compounds). The isolated polyols were then placed in a quartz tube and dried by rotary evaporation (max temp. ~ 50°C). Copper oxide was placed in the tube and higher vacuum was used for more complete drying. The samples were then sealed and combusted to carbon dioxide, and water at 800°C. The carbon dioxide and water were collected with a procedure similar to that of Epstein et al (34). The water was converted to hydrogen by the method of Coleman et al. (35) using a zinc catalyst from J. M. Hayes of Indiana University. The carbon dioxide and hydrogen are then analyzed with 6-60-Nuclide and 3-60-HD Nuclide mass spectrometers. The reported values are uncorrected for terrestrial

carbon and hydrogen. The heavy to light isotope ratio, H/L, for each element (X), reported as per mil (‰), is defined as

$$\delta HX = [\{ (H/L)_{\text{sample}} / (H/L)_{\text{standard}} \} - 1] \times 1000.$$

10. W. Amelung, M. V. Cheshire, G. Guggenberger, *Soil Biol. Biochem.* **28**, 1631 (1997).
11. J. Gilbart, A. Fox, S. L. Morgan, *Eur. J. Clin. Microbiol.* **6**, 715 (1987).
12. J. S. Brimacombe and J. M. Webber in *The Carbohydrates, Chemistry and Biochemistry*, W. Pigman and D. Horton, Eds, (Academic Press Inc., 1972) 479-518.
13. W. Pigman (1957) *The Carbohydrates*. Academic Press Inc.
14. D. J. Des Marais, *Org. Geochem.* **27**, 185 (1997).
15. J. M. De Bruijn, A. P. G. Kieboom, H. Van Bakkum, *Sugar Tech. Reviews* **13**, 21 (1986).
16. W. Pigman and E. F. L. J. Anet in *The Carbohydrates, Chemistry and Biochemistry*, W. Pigman and D. Horton, Eds, (Academic Press Inc., 1972) pp. 165-194.
17. G. Petersson, *Tetrahedron* **26**, 3413 (1970).
18. V. K. Agarwal, W. Schutte, J. M. Greenberg, J. P. Ferris, R. Briggs, S. Connor, C. P. E. M. Van De bult, F. Baas, *Origins of Life* **16**, 21 (1986).
19. G. D. McDonald, L. J. Whited, C. DeRuiter, B. N. Khare, A. Patnaik, C. Sagan, *Icarus* **122**, 107 (1996).

20. G. W. Cooper, M. H. Thiemens, T. Jackson, S. Chang, *Science* **277**, 1072 (1997).
21. W. Langenbeck, *Naturwissenschaften* **30**, 30 (1942)
22. T. E. Bunch and S. Chang, *Geochim. Cosmochim. Acta* **44**, 1543 (1980).
23. Zolensky M. and Mcdween J. Y. (1988), in *Meteorites and the Early Solar System*, J. F. Kerridge and M. S. Matthews, Eds. (Univ. of Arizona, Tuscon, AZ, 1988) pp. 114-143.
24. W. M. Irvine, *Space Sci. Rev.* **90**, 203 (1999).
25. G. A. Jungclaus, G. U. Yuen, C. B. Moore, J. G. Lawless, *Meteoritics* **11**, 231 (1976).
26. J. M. Hollis , F. J. Lovas, P. R. Jewell, *Astrophys. J.* **540**, L107 (2000).
27. R. Hayatsu, M. H. Studier, L. P. Moore, E. Anders, *Geochim. Cosmochim. Acta* **39**, 471 (1975).
28. G. W. Cooper and J. R. Cronin, *Geochimica et Cosmochimica Acta* **59**, 1003 (1995).
29. R. Larralde, M. P. Robertson, S. L. Miller, *PNAS* **92**, 8158 (2000).
30. L. Lowendahl, G. Petersson, O. Samuelson, *Tappi.* **59** (9), 118 (1976).

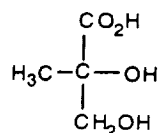
31. G. D. Cody, C. M. O'D Alexander, F. Tera, LPSC XXX, (1999).
32. A. L. Weber, J. Mol. Evol. **35**, 1 (1992).
33. T. P. Mawhinney, J. Chrom. **257**, 37 (1983).
34. S. Epstein, R. V. Krishnamurthy, J. R. Cronin, S. Pizzarello, G. U. Yuen, Nature **326**, 477 (1987).
35. Coleman M. L. and Moore M. P. Anal. Chem. 50, 1594-1595 (1978).
36. The authors would like to acknowledge Art Weber for very helpful discussions on aspects of carbohydrate chemistry; John Cronin for comments on the manuscript and for use of equipment on which the initial Murchison runs were made; Cynthia Asiyo for assistance with figures; and the support of the Exobiology Program of NASA.

	Sugars	Sugar alcohols	Sugar acids	Dicarboxylic Sugar acids
3C	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C} = \text{O} \\ \\ \text{CH}_2\text{OH} \end{array}$ Dihydroxyacetone	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Glycerol	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Glyceric Acid	—
4C	—	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Erythritol and threitol	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Erythronic and Threonic acid	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{CO}_2\text{H} \end{array}$ Tartaric and mesotartaric acid
5C	—	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Ribitol + Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Ribonic Acid + Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CO}_2\text{H} \end{array}$ 2,3,4-Trihydroxy pentane dioic Acid
6C	*	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Glucitol and Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$ Gluconic Acid and Isomers	$\begin{array}{c} \text{CO}_2\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CO}_2\text{H} \end{array}$ Saccharic acid and Isomers

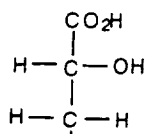
Fig 1A

Deoxy sugar acids

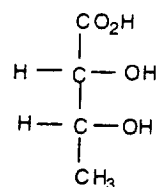
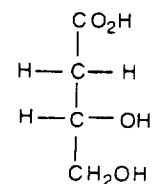
4C



2-Methyl glyceric acid

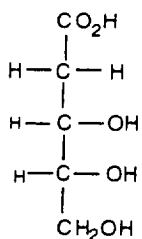


2,4 dihydroxy butyric acid

2,3 dihydroxy butyric acid
(and diastereomer)

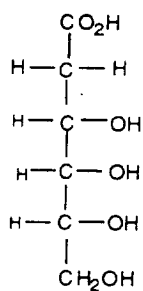
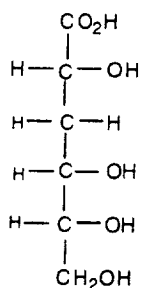
3,4 dihydroxy butyric acid

5C



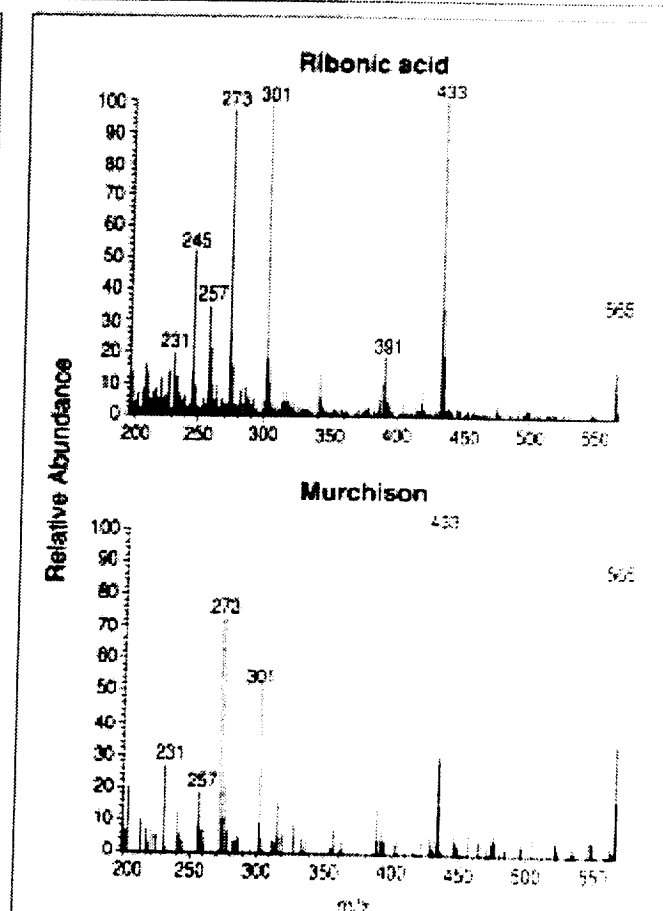
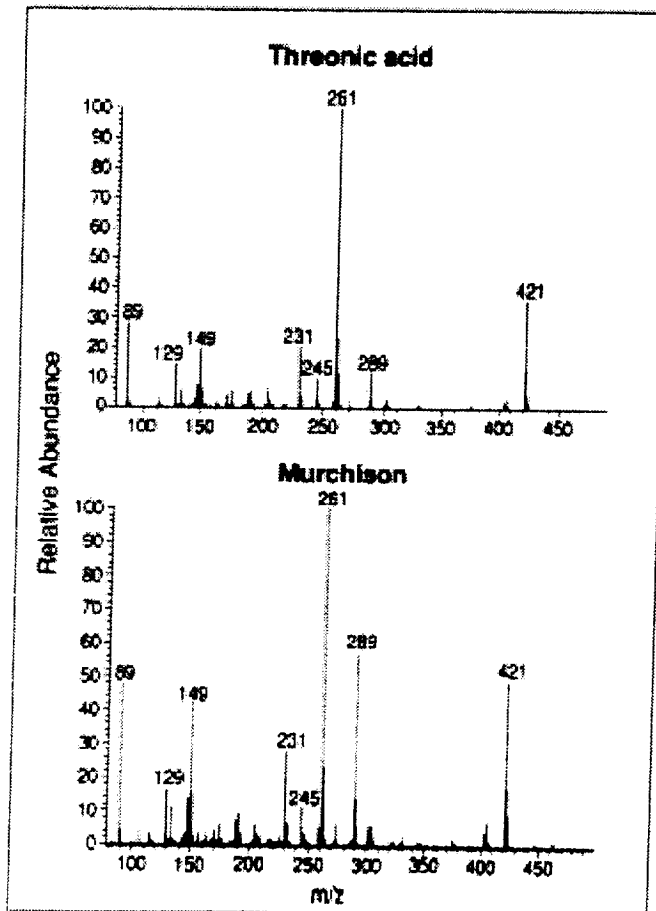
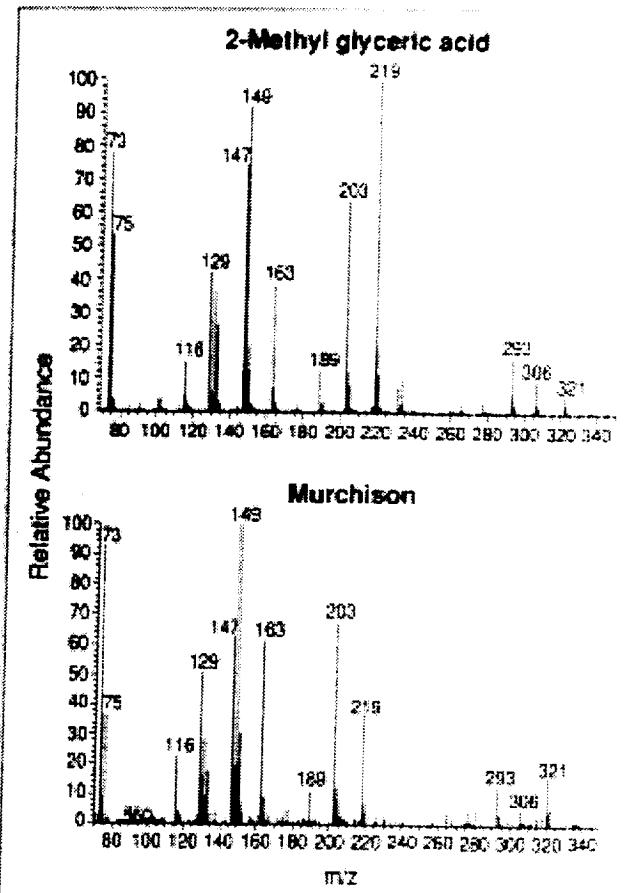
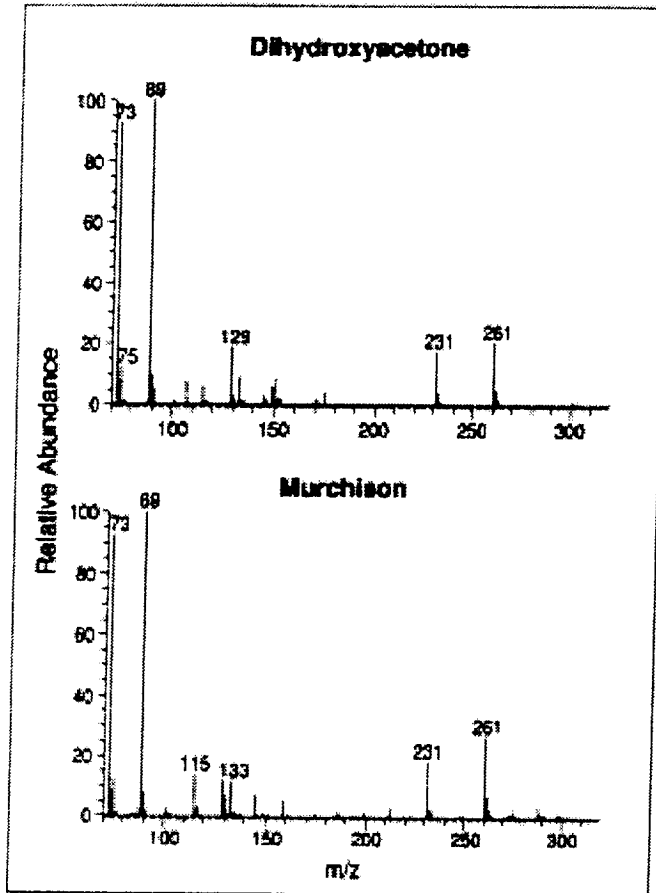
2-Deoxypentonic acids

6C

2-Deoxyhexonic acids[†]

3-Deoxyhexonic acid

Fig 1B



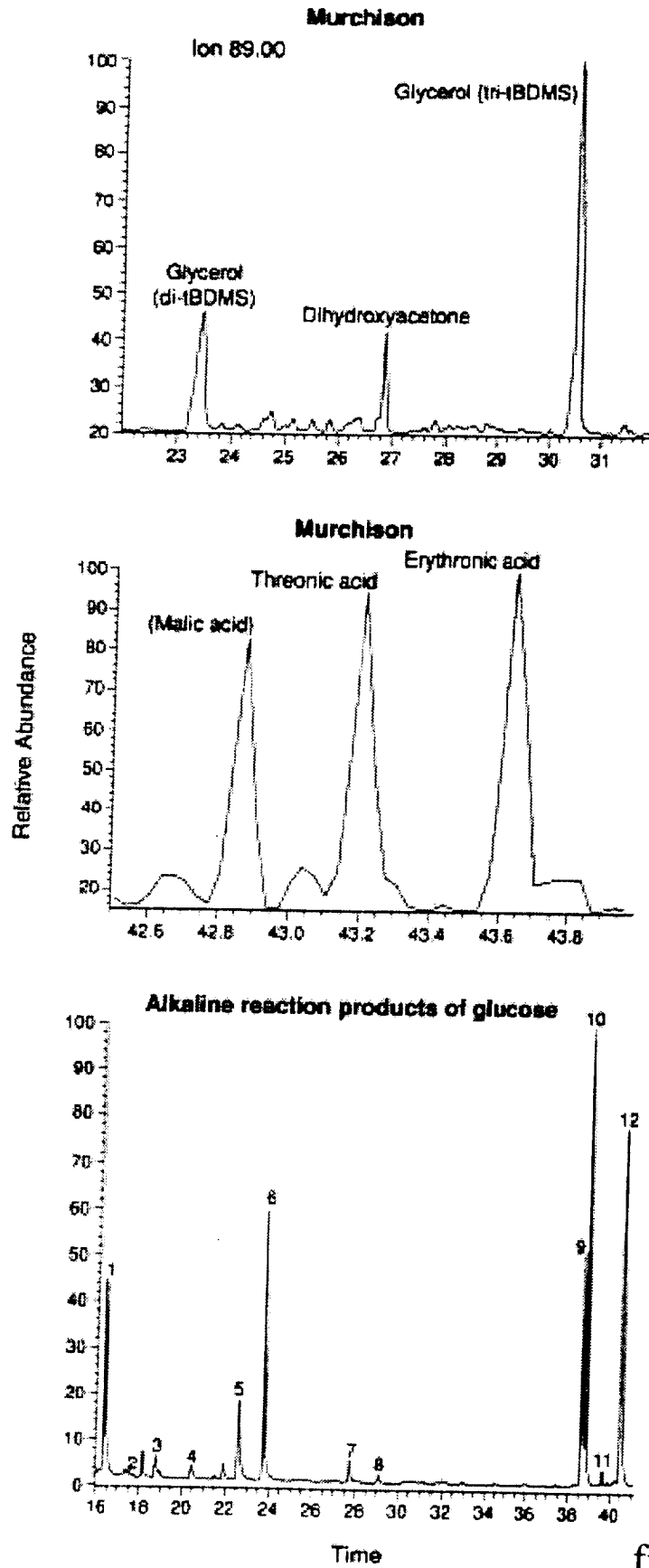


fig 3

